***Table* 4.4** U.S. Production of Alcoholic Beverages, 1965–1978 (in thousands)

Beverage	1965	1972	1978
Sparkling wine, wine gal	6,358	22,864	23,808
Still wine, wine gal	197,257	366,189	473,074
Rectified, proof gallon	92,923	120,815	114,836
Beer, barrel*	108,015	140,327	176,347

*1 barrel equals 31 gal or 117 L.

SOURCE: *Alcohol and Tobacco Summary Statistics*, ATF Publication P1323.1 (4-81), 1978.

RAW MATERIALS. Grains and fruits supplying carbohydrates are the basic raw materials. The variety of grains and fruits employed is wide, changing from country to country, or from beverage to beverage. Russia ferments potatoes and by distillation obtains vodka; similar treatment of the sap of the maguey in Mexico yields pulque; but the world's chief raw materials for fermentations are the cereals, corn, barley, and rice, and grapes.

Beer[23]

Beer and allied products are beverages of low alcoholic content (2 to 7%) made by brewing various cereals with hops, usually added to impart a more-or-less bitter taste and to control the fermentation that follows. The cereals employed are barley, malted to develop the necessary enzymes and the desired flavor, as well as malt adjuncts such as flaked rice, oats, and corn; wheat is used in Germany, and rice and millet in China. Brewing sugars and syrups (corn sugar, or glucose) and yeast complete the raw materials. For beer the most important cereal is barley, which is converted into malt by partial germination. Most brewers buy finished malt from suppliers rather than making their own.

To make malt the barley is steeped in cold water and spread out on floors or in special compartments and regularly turned over for from 5 to 8 days, the layers being gradually thinned as the germination proceeds. At the proper time, when the enzymes are formed, growth is arrested by heat. During growth, oxygen is absorbed, carbon dioxide is given off, and the enzyme diastase is formed. This enzyme is the biological catalyst that changes the dissolved starch into the disaccharide maltose which, after transformation into the monosaccharide glucose by maltase, is directly fermentable by yeast.

The flowchart for beer manufacture in Fig. 4.5 may be divided into three groups of procedures: (1) brewing of the mash through to the cooled hopped wort, (2) fermentation, and (3) storage, finishing, and packaging for market. Mashing is the extraction of the valuable constituents of malt, malt adjuncts, and sugars by macerating the ground materials with 190 to 230 L of water per 100 kg of materials listed in Fig. 4.5 and treating with water to prevent too high a pH, which would tend to make a dark beer. In the pressure cooker, the insoluble

[23]Urang, Debating the Draft, *Chem. Bus.*, May 4, 1981, p. 29. ECT, 3d ed., vol. 3, 1978, pp. 692–735; Marchall et al., Enzymes in Brewing, *Brew. Dig.* **57** (9) 14 (1982); Peppler and Perlman (eds.), *Microbial Technology*, 2d ed., vol. II. Academic, New York, 1979.

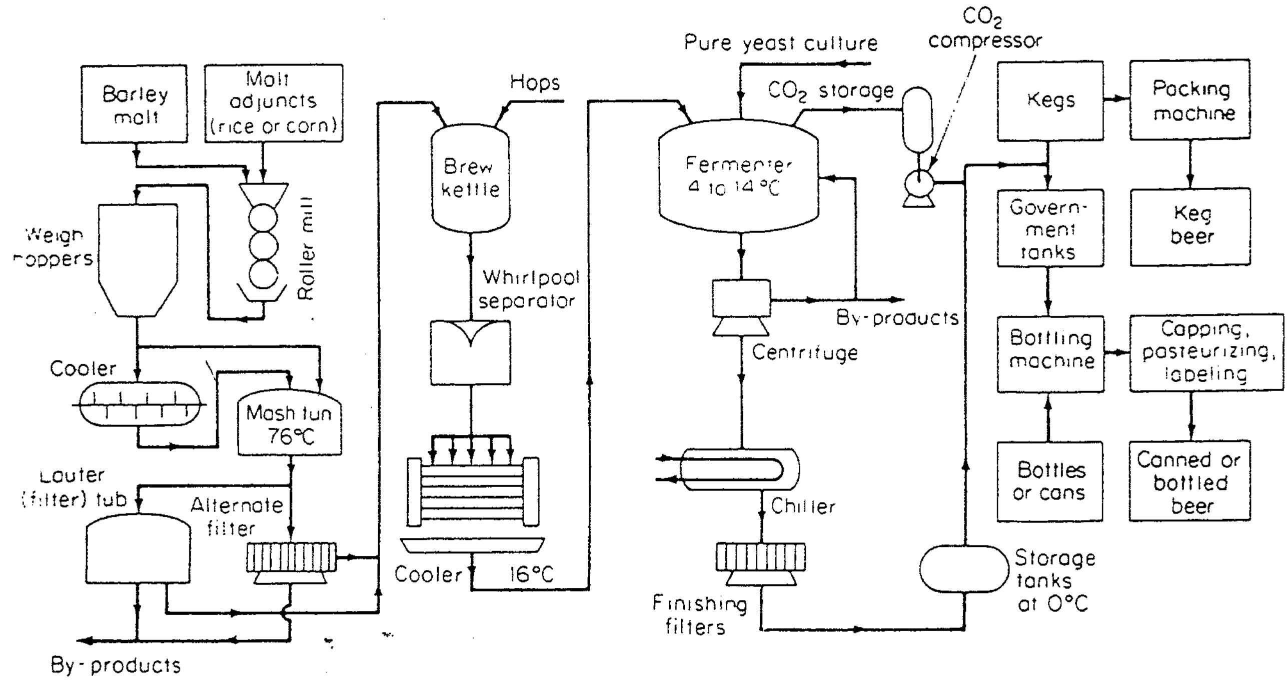

Fig. 4.5. Flowchart for the production of beer.

starch is converted into liquefied starch, and the soluble malt starch into dextrin and malt sugars. The resulting boiling cooker mash, mixed with the rest of the malt in the mash tub, which raises the temperature to 75°C, is used to prepare the brewers' wort.[24] This is carried out in the mash tub. After all the required ingredients have been dissolved from the brewing materials, the entire mash is run from the mash tub to filter presses or the lauter or straining tub, where the wort is separated from the insoluble spent grains through a slotted false bottom and run into the copper wort cooker. For complete recovery of all substances in solution, a spray of decarbonated water at 74°C is rained through the grains. This is called sparging.

The wort is cooked for approximately 1 to 1.5 h, during part of which it is in contact with hops. The purpose of boiling is to concentrate the wort to the desired strength, to sterilize it (15 min) and destroy all the enzymes, to coagulate certain proteins by heat (82°C), to modify its malty odor, and to extract the hop resins' tannin and aroma from the hops, which are added during the cooking process. At the end of the time the spent hops are separated from the boiling wort very quickly in a whirlpool separator. Since the spent hops retain 770 L of wort per 100 kg of hops, they should also be sparged. The wort is then ready to be cooled.

The cooling step is not only to reduce the temperature but also to allow the wort to absorb enough air to facilitate the start of fermentation. The wort is then cooled in a plate heat exchanger to 48°C and then aerated. Slight concentration, due to evaporation, occurs. This operation is performed under controlled conditions to prevent contamination by *wild* yeasts. Frequently, sterilized air is used.

The cooled wort is mixed with selected yeasts in the line leading to the starting tubs, between 285 to 380 g of yeast being used per 100 L of beer. The initial fermentation temperature is 4 to 6°C but, as the fermentation proceeds, the temperature rises to 14°C. This is easily explained by the fact that the conversion of the sugar to carbon dioxide and ethyl

[24]The wort is the liquid resulting from the mashing process, i.e., the extracting and solubilizing of the malt and malt adjuncts. Wort composition varies from 17 to 24% solids by weight for the first wort to approximately 1% solids for the last wort removed by the sparge water.

ohol by the enzymes of the yeast generate 650 kJ per kilogram of maltose converted. The nperature is partly controlled by coolers inserted in the fermentors. The mixture is immed to remove the foreign substances that the evolved carbon dioxide brings to the top. ie carbon dioxide evolved is collected by using closed fermentors and is stored under 17,000 'a of pressure for subsequent use in carbonating the beer.

The yeast gradually settles to the bottom of the fermenting tanks in about 7 to 10 days. ie liquid is very opalescent in appearance, under a cover of foam. As the beer leaves the rmentors, it contains in suspension hop resins, insoluble nitrogenous substances, and a fair nount of yeast. It is then sent to the lagering (aging) tanks where, usually, a second ferentation occurs. The temperature is kept high enough to initiate the second fermentation id then is cooled to 0 to 2°C to lager the beer. Lagering consists of storing at 0 to 2°C for to 4 months. During this time the taste and aroma are improved, and tannins, proteins, and p resins are removed by settling. Highly hopped beers require more lagering time than ers containing less hops. Near the end of the period the beer is saturated with CO_2 at 50 to) kPa.[25] In the United States, public demand favors a brilliant beverage, so the beer is filtered rough a pulp filter under CO_2. About 92 L of beer is produced per 100 L of wort in the arting tubs. After bottling, the beer is pasteurized at 60°C.

Draft beer is not pasteurized. Some bottled beer is not either; it is filtered through fine embranes which remove residual yeast cells and harmful bacteria. This ultrafiltration proices so-called bottled draft beer. Light beer has a carbohydrate content of near zero comared with the usual 4%. This reduces the food content from 600 kJ to about 420 kJ per 355-l bottle. During fermentation the enzyme glucoamylase is added which converts the nonrmentable carbohydrates to glucose. This glucose is then fermented to ethanol.

Beer making has not changed much over the years as brewmasters have been afraid of ianging their beer's taste. However, some new plants have installed automatic wort prouction using hop pellets and using a whirlpool to separate out the hops and sludge. Another inovation which is claimed not to change the final product is high-density brewing wherein ie wort is produced with much less water than usual. This means production can be icreased without increasing equipment. The extra water is added after the preliminary filation. A universal refrigerant-cooled tank to ferment, age, and finish beer in a single tank as also been developed.

Beer contains about 90% water and can be concentrated (dehydrated) to about one-fourth f its original volume. Ice crystals form below the freezing point of water and can be sepaated from the beer concentrate. To reconstitute the beer, water and carbon dioxide are dded.

Vine

Vine has been made for several thousand years by fermentation of the juice of the grape. ike other fermentations, many primitive procedures have been supplanted by improved cience and engineering to reduce costs and to make more uniform products. But now as lways, the quality of the product is largely related to grape, soil, and sun, resulting in a ariation in flavor, bouquet, and aroma. The color depends largely upon the nature of the rapes and whether the skins are pressed out before fermentation. Wines are classified as iatural (alcohol 7 to 14%), fortified (alcohol 14 to 30%), sweet or dry, still or sparkling. For-

[25]The carbon dioxide should be kept free from air, which would interfere with the stability ind quality of the beer. The gas is pumped in close to 0°C and amounts to between 0.36 and).45% of the weight of the beer.

tified wines have alcohol or brandy added. In the sweet wines some of the sugar remains unfermented.

For the manufacture of dry red wine, red or black grapes are necessary. The grapes are run through a crusher, which macerates them but does not crush the seeds, and also removes part of the stems. The resulting pulp, or must, is pumped into 11,000- to 38,000-L tanks,[26] where sulfurous acid[27] is added to check the growth of wild yeast. An active culture of selected and cultivated yeast equal to 3 to 5 percent of the volume of juice is added. During fermentation, the temperature rises, so that cooling coils are necessary to maintain a temperature below 30°C. The carbon dioxide evolved carries the stems and seeds to the top, which is partly prevented by a grating floated in the vat. This allows extraction of the color and the tannin from the skins and seeds. When the fermentation slows up, the juice is pumped out of the bottom of the vat and back over the top. The wine is finally run into closed tanks in the storage cellar, where, during a period of 2 or 3 weeks, the yeast ferments the remainder of the sugar. The wine is given a cellar treatment to clear it, improve the taste, and decrease the time of aging. During this treatment the wine is first allowed to remain quiet for 6 weeks to remove part of the matter in suspension, and then racked for clarification.[28] Bentonite, or other diatomaceous earth, may be used for clearing, 20 to 185 g being stirred into every 100 L of wine. An insoluble precipitate with the tannin is also formed. Extra tannin may also be added, and the wine racked and filtered through diatomaceous earth, asbestos, or paper pulp. The wine is corrected to commercial standards by blending it with other wines and by the addition of sugar, acids, or tannins. It is standard procedure to chill some wines for the removal of argols or crude potassium acid tartate, which constitute the commercial source of tartaric acid and its compounds. This treatment also gives a more stable finished wine. By quick-aging methods it is possible to produce a good sweet wine in 4 months. These methods include pasteurization, refrigeration, sunlight, ultraviolet light, ozone, agitation, and aeration. The wine may be held at about freezing for 3 weeks to a month, and a small amount of oxygen gas bubbled in. Then the wine is racked, clarified, and further filtered in the usual manner. The wine trade is large and growing rapidly in the United States.

Distilled Spirits

Various fermented products, upon distillation and aging, yield distilled liquors. Figure 4.6 shows the flowchart for whiskey and gin, and Table 4.5 presents statistics. Brandy is distilled from wine or from the *marc*, which is the pulp left by racking or straining. Making a beer[29] from a grain mixture containing at least 51% corn and distilling and aging it yields bourbon

[26]In many modern American wineries these tanks are even larger and are constructed of concrete.

[27]Potassium or sodium metabisulfite and/or sodium bisulfite may also be used.

[28]During this and the following period the new wine undergoes a complicated series of reactions, resulting in the removal of undesired constituents and development of the aroma, bouquet, and taste. Oxidation takes place, as well as precipitation of proteins and argols, and esterification of the acids by alcohols. Certain modifications of this process are presented in Chemical Technology, Key to Better Wines, *Chem. Eng. News* 51 (27) 44 (1973); Chemistry Concentrates on the Grape, *Chem. Eng. News* 51 (26) 16 (1973).

[29]The yeast in this fermentation is grown in the presence of lactic acid to ensure proper strain and to secure the desired quality of the whiskey.

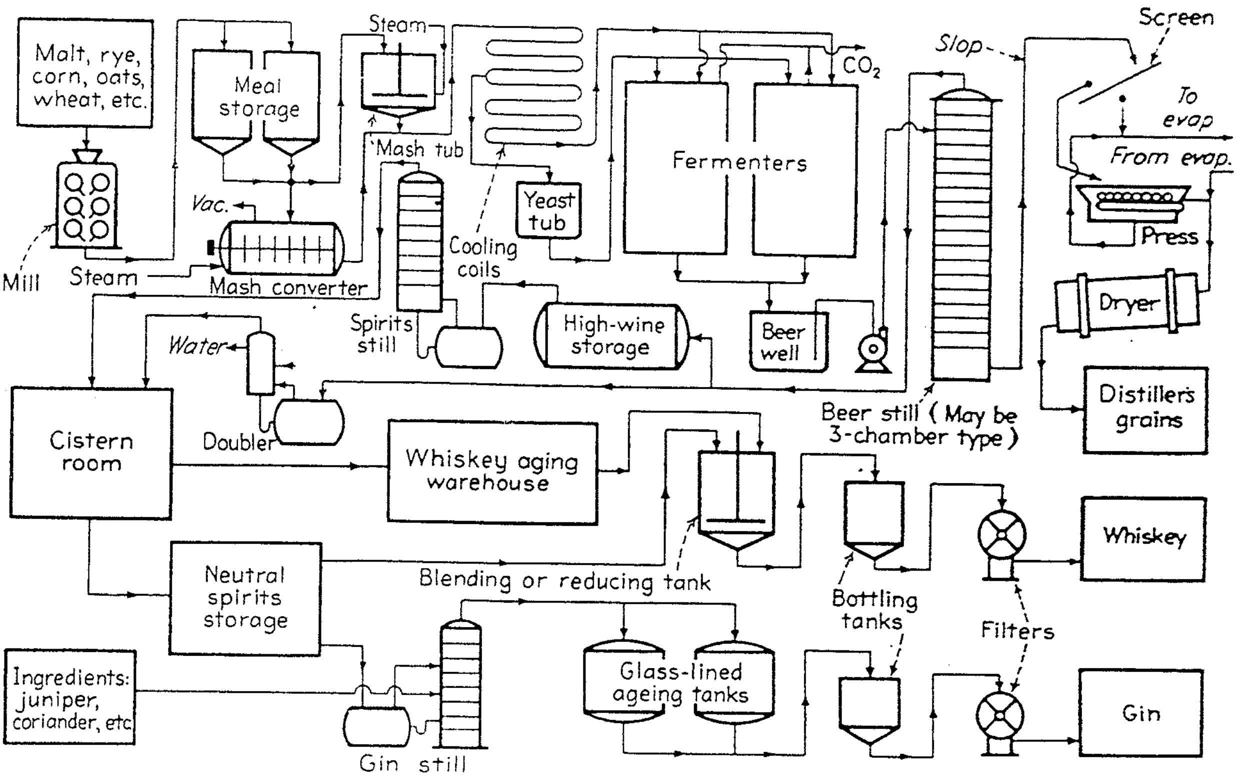

Fig. 4 .6. Flowchart for the production of distilled liquors.

whiskey. Similarly, rye whiskey must start with 51% rye in the grain to be mashed and fermented. Scotch whisky (never spelled with an "e" as in all other whiskey) comes only from Scotland and uses barley dried with peat which gives it its distinctive flavor. By inspecting the flowchart in Fig. 4 .6 in the light of Fig. 4 .1 and 4 .5, and the description accompanying them, the procedures in Fig. 4 .6 for distilled liquors will be clear. In modern liquor plants the equipment, up to the stills, is of steel, and the stills are of copper or stainless steel. By law, the aging of bourbon or rye whskey of claimed age must take place in charred new white-oak barrels of approximately 190 L. These are kept in bonded warehouses at 18 to 30°C and at a preferred humidity of 65 to 70%, usually for 1 to 5 years. During this time evaporation of the contents takes place, largely through the ends of the barrel staves. By reason of more

***Table* 4 .5** U.S. Net Production of Distilled Spirits (in thousands of proof gallons)

	1970	1975	1980
Whiskey	112,882	140,818	103,860
Brandy	12,353	15,176	14,635
Rum	617	5,594	20,311
Gin	26,922	28,822	24,583
Vodka	20,079	33,483	26,958
Spirits	85,639	83,580	97,519
Total	258,441	307,472	287,864

SOURCE: *Annual Statistical Review, 1980,* Distilled Spirits Industry: Distilled Spirits Council of the United States.

rapid capillary travel and osmosis of the smaller water molecules in comparison with the alcohol molecules, an increase in the percentage of alcohol is found in the barrel contents. The government shrinkage allowance is approximately 8 percent the first year, 4 percent the second year, 4 percent the third year, and 3 percent the fourth year. If the shrinkages are exceeded (and this is often the case), the manufacturer must pay a tax on the excess, but with the best cooperages under the best conditions these allowances can just be met. The distillate from the spirit still is under 160 proof and is subsequently diluted upon barreling to 100 to 110 proof. It is not pure alcohol but contains small amounts of many different constituents, generally classed together as congenerics, which by their reaction with each other or the alcohol, or by their absorption, both catalyzed by the char of the wood, help greatly in imparting the whiskey flavor and bouquet. The aging whiskey also extracts color and other products from the charred white oak. Changes of a like nature occur similarly in aging brandy and rum. Here, as in other divisions of the fermentation industries, skill and scientific knowledge aid in the production of a palatable product. By law, whiskey must be fermented from whole grains, so that the germs (containing the corn oil) and the husks are suspended in the liquor from the beer still in whiskey manufacture. This discharge liquor is known as slop, or stillage. As shown in Fig. 4.6, it is treated to recover the values by separating the solids from the liquid slop. After vacuum evaporation of the liquid portion, it is added to the solids, and the mixture is dried in rotating steam-heated dryers to produce distillers' grains, a valuable cattle feed.

BUTYL ALCOHOL AND ACETONE

Until World War I, all the acetone produced was made by the dry distillation of calcium acetate from pyroligneous acid. Under the stimulus of the wartime demand for acetone for the manufacture of smokeless powder, Weizmann[30] developed a process utilizing the fermentation of starch-containing grains to yield acetone and butyl alcohol. Commercial Solvents Corp. was organized, and it built and operated two plants in the Corn Belt to ferment corn, using *Clostridium acetobutylicum* bacteria. This fermentation, however, gave 2 parts butyl alcohol to 1 part acetone and, until the development of fast-drying nitrocellulose lacquers, particularly for the automotive industry, there was virtually no market for the butyl alcohol produced. Then conditions became reversed, butyl alcohol becoming the important commodity and acetone the by-product. This better sale of first one product and then another is characteristic of industries in the chemical field, where more than one substance results from a process and reflects the changing demand that accompanies a growing and dynamic industry. New cultures feeding on molasses were developed, which also gave a more desirable solvent ratio (approximately 3 parts butyl alcohol to 1 part acetone). Higher costs for molasses and grain now have given the synthetic processes such a dominant position that the latter fermentation process has stopped. Today, acetone is coproduced with phenol by the oxidation of cumene or dehydrogenation of isopropyl alcohol. It is used as a solvent and in fabricating plastics. About 1×10^9 kg was produced in the United States in 1981.[31]

RIBOFLAVIN. Riboflavin was first produced commercially as a by-product of acetone–butyl alcohol fermentation, but the concentration was low. Several greatly improved biological processes have been dominated by the lower-cost synthetic process presently used

[30] Brit. Patent 4845 (1915); U.S. Patent 1,315,585.

[31] [illegible]

VINEGAR AND ACETIC ACID

The aerobic bacterial oxidation (by the genus *Acetobacter*) of alcohol to dilute acetic acid (8%) is another ancient procedure, furnishing vinegar, a flavored acetic acid solution, fermented from wine, cider, malt, or dilute alcohol. If pure dilute alcohol is fermented, pure dilute acetic acid results. The yield is 80 to 90% of theory. Air[32] must be supplied, as these formulations indicate:

$$2C_2H_5OH + O_2 \rightarrow 2CH_3CHO + 2H_2O \quad 2CH_3CHO + O_2 \rightarrow 2CH_3COOH$$

Since these reactions are exothermic, either the alcohol can be slowly trickled through the apparatus, letting the heat dissipate, or it can be recirculated with special cooling. If cider, malt, or wine is fermented, the acetic acid content of the resulting vinegar rarely exceeds 5% because of limitations of the sugar content; if dilute alcohol is the raw material, the acetic acid may rise to 12 or 14% at which acidity the bacteria cease to thrive. If a fruit juice is turned to vinegar, certain esters are formed, varying with the raw material and thus imparting a characteristic flavor. Synthetic acetic acid is made from ethylene, or by treating methanol with carbon monoxide.

CITRIC ACID

Citric acid is one of our most versatile organic acids. Its major use is as an acidulant in carbonated beverages, jams, jellies, and other foodstuffs. Another large outlet is in the medicinal field, including the manufacture of citrates and effervescent salts. Industrial uses, relatively small, include citric acid as an ion-sequestering agent buffer and acetyl tributyl citrate, a vinyl resin plasticizer. Citric acid is meeting competition from other organic acids, for example, fumaric, maleic, and adipic.

Except for small amounts (less than 7 percent) produced from citrus-fruit wastes, citric acid is manufactured[33] by aerobic fermentation of crude sugar or corn sugar by a special strain of *Aspergillus niger*, following the classical research by Currie. The overall reactions are

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O + 3O_2 \rightarrow 2C_6H_8O_7 + 4H_2O$$

$$\underset{\text{Dextrose}}{C_6H_{12}O_6} + 1\tfrac{1}{2}\,O_2 \rightarrow \underset{\text{Citric acid}}{C_6H_8O_7} + 2H_2O$$

The fermentation changes sugar and dextrose, straight-chain compounds, into branched chains. An earlier shallow-tray fermentation process was abandoned because of the expensive manual processing and the development of the submerged process.

The submerged process for the manufacture of citric acid is depicted in Fig. 4.7, and this

[32]Too much air causes losses because of further and undesired oxidation; ECT, 3d ed., vol. 6, 1979, pp. 150–173.

[33]Currie, The Citric Acid Fermentation of *A. niger*, *J. Biol. Chem.* 31 15 (1917).

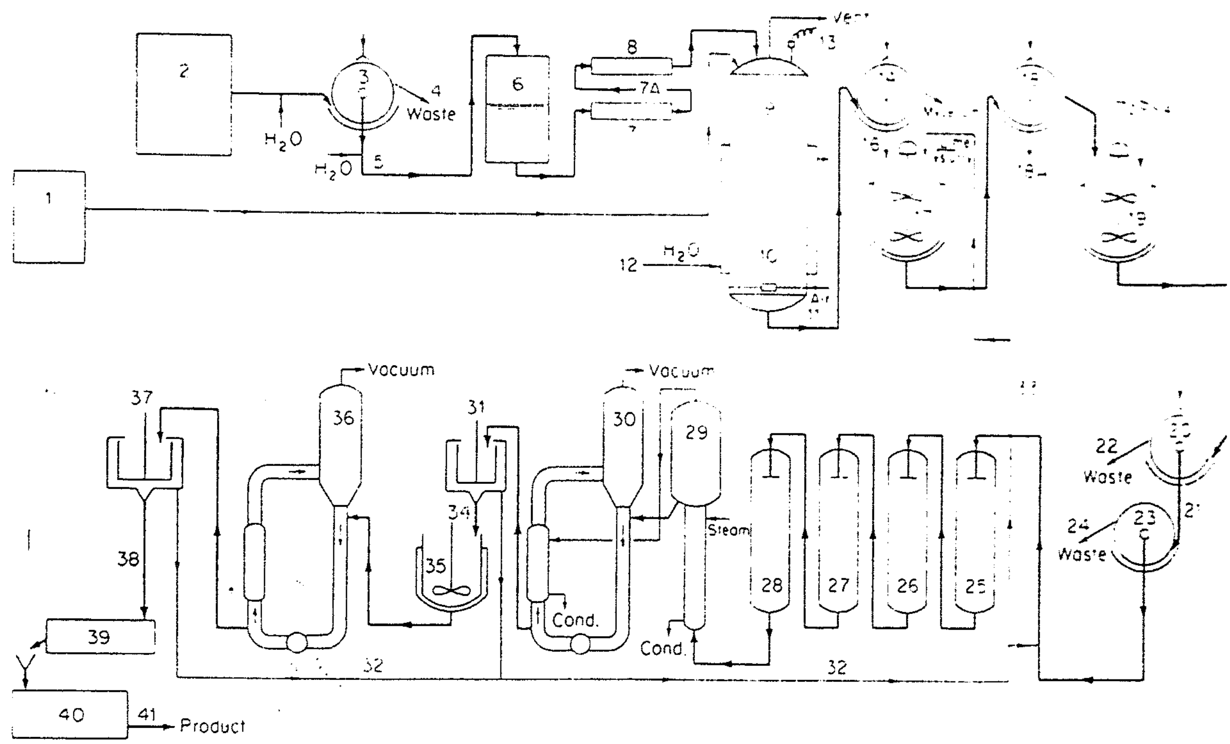

Fig. 4 .7. Flowchart for citric acid production. The purification of the dextrose glucose syrup is fundamental (nos. 2 through 8), involving a rotary vacuum filter (3) to remove suspended or precipitated solids after partial dilution. This is followed by a cation-exchange cell (6) for trace-element reduction and a flash pasteurization heater (7), holding loop (7a), and syrup cooler (8). The syrup is pumped into the fermentor (9) plus inoculum (1). The pH adjustment is made and nutrients added. Sterile air (11) from filters and flowmeters is sparged (10) into the fermentor (9). The fermentation process for the production of citric acid is, in its simplest terms, the conversion of a molecule of a hexose sugar to a six-carbon molecule of citric acid (9). The purification and recovery of the resultant acid are then basically an application of the lime-sulfuric scheme first used by Scheele in 1784. Today's methods involve first separating off the mycelium (14) from the broth, which contains the citric acid (16), liming it with milk-of-lime slurry (17), filtering off and washing the resultant calcium citrate (18), and finally decomposing the citrate with sulfuric acid (19). The calcium sulfate formed from this decomposition is filtered off as a waste by-product (20, 23). The more modern plants of today perform these three filtrations on some form of rotary vacuum filter. The further purification of the decomposed liquor from the sulfuric decomposition is variable from manufacturer to manufacturer. This figure indicates treatment with granular carbon in fixed beds (25, 26), followed by demineralizing beds containing cation- and anion-exchange resins (27, 28). Double-or triple-effect evaporators (29) feed a separate crystallizer (30) and centrifuge (31). The mother liquor is recycled between feed to carbon cells (32) or to a liming tank (33). The damp citric acid crystals are remelted (35) and vacuum crystallized (36). This is followed by centrifuging (37), drying (39), size classification (40), and packaging (41). The degree of purity of the initial sugar source going into the fermentation can be a factor in determining the amount of purification necessary and the need for recrystallizing the final product. *(Miles Laboratories, Inc.)*

may be broken down into coordinated sequences of biochemical conversions with the aid of *A. niger* and various unit operations and chemical conversions. A selected strain of *A. niger* is grown from a test-tube slant through to a seed tank, or inoculum. This growth may take 36 to 48 h. For sequential steps see the description below Fig. 4 .7.

Special strains of yeast, *Candida guillier mondii* and *Candida lipolytica*, have been developed to produce citric acid. *C. lipolytica*[34] produces it from paraffin in a continuous process.

[34] U.S. Patent 4,014,742.

LACTIC ACID

Lactic acid, 2-hydroxypropionic acid, is one of the oldest known organic acids. It is the primary acid constituent of sour milk, where it derives its name, being formed by the fermentation of milk sugar (lactose) by *Streptococcus lactis*. Commercially, lactic acid is manufactured by controlled fermentation of the hexose sugars from molasses, corn, or milk. Lactates are made by synthetic methods from acetaldehyde and lactonitrile, a by-product of Monsanto's[35] acrylonitrile operation. It has been only since 1930 that lactic acid has been produced commercially from the milk by-product whey. About 1×10^9 kg of dry whey is produced annually from cheese or casein production, and about half is wasted.[36] The technical grade is employed for deliming leather in tanning. Edible grades are used primarily as acidulants for a number of foods and beverages. The small amount of lactic acid remaining is converted into plastics, solvents, and certain other chemical products. The USP grade is an old, well-established standard pharmaceutical.

MISCELLANEOUS COMPOUNDS

MONOSODIUM GLUTAMATE. The amino acid glutamic acid may be prepared synthetically, but chemical preparation produces a racemic mixture. Since only the sodium salt of the naturally occurring L-glutamic acid is desired for food flavor enhancement, this necessitates an expensive resolution step. L-Glutamic acid can be obtained directly from fermentation of carbohydrates with *Micrococcus glutamicus* or *Brevibacterium divaricatum*. Many patents have been issued on variations of the process as this is one of the largest volume compounds produced by fermentation.[37]

L-LYSINE. L-Lysine may be formed by microorganisms acting on carbohydrates. The usual organisms are *Micrococcus glutamicus*, *Brevibacterium flavum*, *Corynebacterium acetoglutamicum*, and *Microbacterium ammoniaphilum*. Each of these organisms requires special conditions and/or special additives to produce the product in good yields.

DIHYDROXYACETONE. Dihydroxyacetone ($HOCH_2COCH_2OH$) is made by the action of sorbose bacterium fermentation of glycerin.[38] This is an ingredient of suntan lotion that creates an artificial tan. It is also valuable as a chemical intermediate and as a catalyst in butadiene-styrene polymerization. Fatty acid esters of the hydroxyl groups are excellent emulsifying agents.

PHARMACEUTICAL PRODUCTS. The pharmaceutical industry has long employed fermentation (biosynthesis) to manufacture some of its most important medicaments. See Chap. 40, where fermentation is presented for antibiotics, biologicals, vitamins, and hormones. Controlled microorganisms are a most important chemical processing agent and assist in performing very complicated chemical reactions, in many cases more economically than purely

[35]Synthetic Lactic Acid, *Ind. Eng. Chem.* 51 (2) 55 (1964); *Chem. Eng.* 71 (2) 82 (1964).

[36]Fermentation Process Turns Whey into Valuable Protein, *Chem. Eng.* 82 (6) 36 (1975).

[37]Gutcho, *Chemicals by Fermentation*, Noyes, Park Ridge, N.J., 1973.

[38]U.S. Patent 2,948,658

chemical conversions. This is especially true for complicated structural changes to make derivatives of natural steroid hormones.

Detailed flowcharts (Fig. 6.5) are given for three antibiotics, penicillin, streptomycin, and erythromycin. Chemical synthesis is given in Chap. 6 for riboflavin, as well as fermentation processes.

ENZYMES

Tables 4.1 and 4.6 list certain enzymes, organic catalysts formed in the living cells of plants and animals, which are essential in bringing about specific biochemical reactions in living cells. Enzymes can be classified by their method of activity.[39]

Catalytic function	Name
Oxidation-reduction	Oxidoreductases
Group transfer	Tranferases
Hydrolysis	Hydrolases
Group removal	Lyases
Isomerization	Isomerases
Joining of molecules	Ligases

Over 3000 enzymes have been extracted and purified. An enzyme generally can be stored dry and cool for several months or even years, but in solution it may lose its catalytic ability in minutes or hours. Efforts to stabilize the catalytic ability of enzymes have resulted in their immobilization on a solid support which makes them more resistant to pH and temperature

[39]ECT, 3d ed., vol. 9, 1980, pp. 148–224.

Table 4.6 Typical Industrial Enzymes Sold Today

Enzyme	Application
Proteases	Cheesemaking
	Digestive aids
	Meat tenderizing
	Beer chillproofing
	Cereal syrups manufacture
	Leather manufacture
Carbohydrases	Starch hydrolysis
	Sucrose inversion
	Fruit juice and vinegar clarification
Nucleases	Flavor control
Hydrolytic enzymes	Destruction of toxic or undesirable components in food
Oxidases	Oxidation prevention and color control in food products
	Clinical diagnostics

SOURCE: *CHEMTECH*, 3 677 (1973); 4 47, 309, 434 (1974).

changes. When immobilized, an enzyme may remain active for months, even when suspended in water.

Several methods are available for immobilizing enzymes. The oldest is adsorption on an ion-exchange resin, but in use the enzyme is slowly leached into the solution. To eliminate loss during use the enzyme can be intermolecularly cross-linked with the support, covalently bonded to the surface of a chemically reactive support, or trapped in the interstices of a polymer by copolymerization with a suitable monomer.

The amylases are the most important of the carbohydrases. One of the newer applications is the use of glucose isomerase to change glucose to fructose. These enzymes are often made by submerged fermentation, starting with corn-steep liquor and cornstarch. This mixture, after proper sterilization and cooling, is inoculated with *Bacillus subtilis* and fermented. The amylase can be isolated by precipitation with isoamyl alcohol and centrifugation. More amylases are commercially produced than any other enzyme.

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Chapter 5

Pulp and Paper Industries

Cellulose is not only the most abundant organic substance available, it is a major component of woody plants and is constantly replaceable. Its conversion to paper products is the function of the pulp and paper industries which manufacture thousands of useful items from it. The national per capita production of pulp and paper was approximately 300 kg in 1981. The industry employs about 650,000 people and uses over 10,000 scientists and engineers. The manufacturing processes are complicated and difficult to control. The use of digital control devices has increased the efficiency of the industry and generally improved the economy of operation. Without good control devices, modern paper-making machinery could not function. Papermaking consumes many chemicals as shown in Table 5.1. The pulp and paper industries are not only consumers of large quantities of chemicals but are the largest energy users in the country, for this is an energy-intensive business.

HISTORICAL.[1] Writing paper first appeared between 2500 and 2000 B.C., made from a tall reed called papyrus which grows along the Nile river in Egypt. Strips from the reed were glued together with starch. This sheet was superior to calf and goatskin parchments, clay bricks, waxed boards, and other writing materials available at that time. The Chinese invented good processes for paper manufactured from bamboo and cotton about A.D. 105 and continue to make good paper by hand today. Southern Europe learned of the process and began to manufacture rag paper near the end of the fourteenth century. English manufacturers became established in the seventeenth century, and a paper mill was established in the United States in 1690. At this time all European paper was made from cotton and linen rags. Book printing began with Gutenberg's bible and greatly increased the demand for paper.

About 1750 the beater was developed and adopted in Holland, hence it became the Hollander. In 1799, a Frenchman, Robert,[2] invented the process for forming sheet paper on a moving wire screen. During evolution and improvement, this became today's Fourdrinier machine. In 1809 the cylinder machine was invented by Dickinson and forced the Fourdrinier into the background, but by 1830 the Fourdrinier's superiority for making fine papers was established. In 1826, steam cylinders were first used for drying and the first Fourdrinier was received in the United States in 1827. Paper demand increased with lower prices and

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[1]Hunter, *Papermaking, the History and Techniques of an Ancient Craft,* Dover, New York, 1974; Britt (ed.), *Handbook of Pulp and Paper Technology,* 2d ed., Van Nostrand Reinhold, New York, 1970.

[2]Clapperton, *The Paper-Making Machine. Its Invention, Evolution, and Development,* Pergamon, Oxford, 1967.

Table 5.1 Composition of a Metric Ton of Paper

The following ingredients are necessary to produce an average metric ton of paper, representative of a variety of grades.

Water	133,000 L	Power	4752 MJ
Sulfur	15.5 kg	Talc	28 kg
Magnesium hydroxide	20 kg	Synthetic fillers	10.5 kg
Lime	176.5 kg	Alum	14 kg
Salt cake (Na_2SO_4)	33 kg	Clay	66 kg
Caustic soda	29 kg	Rosin	6 kg
Chlorine	54 kg	Dye and pigments	8 kg
Starch	53 kg	Capital investments per metric ton	$704
Wood	4 m^3	Work hours per metric ton	12.4
Fuel 686 L of oil or 1 t of coal			

SOURCE: The Wisconsin Paper Council, see *Pap. Trade J.* 166 (16) 41 (1982)

advancing general education, so a rag scarcity developed. Keller of Saxony developed a mechanical process for making pulp from wood, but the quality of the paper produced was low. The soda process for making pulp from wood was developed by Watt and Burgess in 1851. In 1857, the American chemist, Tilghman was granted the basic patent (U.S. 70,485) for the sulfite process, which produced good, readily bleachable pulp. The kraft process (from the German word kraft = strong) resulted from basic experiments conducted by Dahl in 1884 in Danzig. This process is commonly also referred to as the sulfate process because sodium sulfate is used as a make-up chemical for the cooking liquor. The dissolving agent, however, is not Na_2SO_4. In 1909, the sulfate process was introduced into the United States. At that time, pulp production was divided into 48 percent mechanical, 40 percent sulfite, and 12 percent soda.

The sulfate process has come to dominate the industry (see Table 5.2), and in 1981 the distribution had become 10.5 percent mechanical and thermomechanical, 3.5 percent sulfite,

Table 5.2 U.S. Production of Wood Pulp (thousands of metric tons)

	1980		1981	
	Air-Dried Weight,	Distribution, %	Air-Dried Weight,	Distribution, %
Bleached sulfite	1,324	3.0	1,272	2.8
Unbleached sulfite	349	0.8	362	0.8
Bleached and semibleached sulfate/soda	17,237	38.6	18.198	39.6
Unbleached sulfate/soda	17,773	39.8	17,757	38.6
Semichemical	3,652	8.2	3,560	7.7
Groundwood and thermomechanical	4,324	9.7	4,826	10.5
Paper grade wood pulp, total	44,659	100	45,975	100
Dissolving and special alpha pulp for chemical conversion	1,327		1,201	
Total	1,368		1.239	

SOURCE: American Paper Institute.

78.2 percent sulfate, and 7.7 percent semichemical.[3] Pulp manufacture gradually developed into an industry of its own, serving other industries as well as paper manufacture. Rayon, cellulose esters and ethers, and cellulose nitrate for both plastic and explosive use have become commercially important and consume much high-quality wood pulp. The control and utilization of the industry's by-products have required much attention (Chap. 32). The creation of useful products from lignin and waste liquors represents increased income for the industry and a solution to the stream pollution problem, but the development has just really begun and most of the by-products are still regarded as wastes and burned.

USES AND ECONOMICS. In 1980 the production of paper and paperboard in the United States was about 59.7×10^6 t.[3a] The consumption of newsprint alone was estimated at 10.1×10^6 t and 61,000 t of wood pulp were produced. The United States consumes about half of the world's paper production.

MANUFACTURE OF PULP

Before paper can be made from wood, the cellulose fibers must be freed from the matrix of lignin which cements them together. The fibers may be separated by mechanical procedures or by solution of the lignin by various chemicals (Table 5.3). The pulp thus formed has its fibers recemented together to form paper when suitable additives are used. In 1981, 89.5 percent of the pulping was carried out by chemical means. Pulp made by mechanical or thermomechanical means is inferior in quality to that produced chemically; much of it goes into newsprint. The kraft process dominates the field with semimechanical means a poor second.

RAW MATERIALS. Cotton and linen rags, once the major sources of fibers for paper have now been largely supplanted by fibers from wood. About 20 percent of the pulp used in the United States is recycled, and Europe and Japan recycle an even larger percentage. Both hard (deciduous) and soft (coniferous) wood are used to make pulp, but softwood is preferred because the fibers are longer. Bark cannot be used because it is not fibrous and is difficult to bleach. Bark is removed at the pulp mill by one of two debarking methods. The first abrades off the bark utilizing friction between pulpwood logs tumbled about in a rotating, cylindrical drum. Stationary drums using cams to move the logs about utilize the same principle. The bark is carried away in a stream of water, strained out, and usually burned. One company in Oregon recovers wax and corklike material from bark. The more generally used method is hydraulic debarking. Here a jet of high-pressure water (at about 10 MPa) is directed tangentially to the log and strips away the bark cleanly, breaks it up, and sluices it away. Recovered bark is often compressed before burning to reduce the water content and facilitate combustion.

PULPING PROCESSES. All processes used for pulping have the same goal—to release the fibrous cellulose from its surrounding lignin while keeping the hemicelluloses and celluloses intact, thereby increasing the yield of useful fibers. The fibers thus obtained are naturally colored and must be bleached before they can be used for paper. Here again, the goal is to obtain good color without degradation and loss of yield.

There are many processes and variations of basic processes which can be used for making

[3] *Wood Pulp and Fiber Statistics*, American Paper Institute, 1981.

[3a] t = 1000 kg.

***Table* 5.3 Comparison of Three Types of Chemical Pulp**

Type of Process	Kraft, or Sulfate, Pulp (Alkaline)	Sulfite Pulp (Acid)	NSSC
Cellulosic raw material	Almost any kind of wood, soft or hard	Coniferous; must be of good color and free of certain phenolic compounds	Hardwood chiefly used, some softwood *(small chip size, fiberized)*
Principal reaction in digester	Hydrolysis of lignins to alcohols and acids; some mercaptans formed	RC:CR′ + $Ca(HSO_3)_2$ → $(RCHCR'SO_3)_2Ca$	Lignin sulfonation and hemicellulose hydrolysis lead to formation of acetate and formate.
Composition of cooking liquor	12.5% solution of NaOH, Na_2S, and Na_2CO_3. Typical analysis of solids: 58.6% NaOH, 27.1% Na_2S, 14.3% Na_2CO_3. Dissolving action due to NaOH and Na_2S. Na_2CO_3 inactive and represents the equilibrium residue between lime and Na_2CO_3 in the formation of NaOH.	7% by weight SO_2, of which 4.5% is combined as sulfurous acid and 2.5% as calcium or $Mg(HSO_3)_2$. Cooking 1 t of pulp requires 175 to 220 kg of SO_2 and 55 to 68 kg of MgO. Recent significant trend toward use of $Mg(OH)_2$, NH_4OH as base to speed lignin solution	Na_2S buffered with Na_2CO_3 bicarbonate, or kraft green liquor. Concentration of 90–100 g/L of Na_2S. Cooking liquor does *not* complete freeing of fibers, but mechanical treatment does
Cooking conditions	Time 2–5 h; temp. 170–176°C; pressure 660–925 kPa	Time 6–12 h; temp. 125–160°C or higher; pressure 620–755 kPa	Time 48–36 min; corrugating-grade pulp from mixed hardwoods 12–15 min; temp. 160–180°C, pressure 660–1100 kPa